Ni-B/TiO₂ Amorphous Catalyst Used in Heavy Arenes of Petrochemicals Hydrogenation

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Abstract: A supported Ni-B/TiO₂ amorphous catalyst was prepared by impregnation and reduction. It was characterized by XRD, SAED, DSC, XPS, *etc.*. The catalytic activity of catalyst was measured through the hydrogenation of heavy arenes in petrochemicals for the first time.

Keywords: Hydrogenation, heavy arenas, petrochemicals, Ni-B/TiO₂ amorphous catalyst.

The various distillation of petroleum contains arenes. For environmental protection, the hydrogenation of arenes becomes important. The amorphous alloy is a new class of material with special catalytic properties for reduction arenes¹⁻⁴. In this paper, we prepared the Ni-B/TiO₂ and Ni-B/Al₂O₃ amorphous catalysts by impregnation and reduction by KBH₄ solution. Their catalytic activities for hydrogenation arenes were tested by the hydrogenation of 1,3,5-trimethylbenzene (TMB) in the continuous flow fix-bed reactor controlled by computer. To our knowledge, this kind of catalysts were not reported in literatures.

Experimental

Catalyst preparation

Supported Ni-B/TiO₂ amorphous catalyst was prepared with an impregnate-reduction method^{5,6}. The reductive Ni-B/TiO₂ was obtained by hydrogenation at 473 K for 2.0 h.

Catalyst characterization

The bulk composition of the catalysts were analyzed by ICP-9000 (N+M) inductively coupled plasma. The amorphous characters were determined by X-ray diffraction (XRD) on a Rigaku D/max-2500 powder diffractometer with Cu K α radiation, and their crystallization process was followed by differential scanning calorimetry (DSC) conducted on a NETZSCH-Geratebau GmbH Thermal Analysis under N₂ atmosphere at

the heating rate of 10 K/min. X-ray photoelectron spectroscopy (XPS) measurements were taken by a PHI-5300 ESCA system with Mg K α radiation. The C1s line of contaminant carbon on the catalyst surface at 284.6 eV was taken as an internal standard and was used to correct possible deviations caused by electronic charges of the samples.

Activity test

The activities of amorphous catalysts were evaluated by the hydrogenation of heavy arenes in the continuous flow fix-bed reactor controlled by computer. The reaction products were analyzed by using HP G 1800A chromatogram-mass spectrum. The feed liquid was TMB (10 v.%) diluted with cyclohexane (90 v.%) or 200# concoctive oil (provided by Tianjin Petrochemicals Company and the heavy arenes was 10.5% by mole).

Results and Discussion

The XRD patterns of TiO_2 and Ni- B/TiO_2 are almost the same. The typical amorphous ring on the selected area electron diffraction (SAED) pattern confirmed the amorphous state of the Ni- B/TiO_2 . This showed that the amorphous Ni-B supported on TiO_2 cannot be detected by XRD because of its high dispersion and low loading (the nickel content was only 2.97% by weight). There were two exothermic peaks on the DSC curve of Ni- B/TiO_2 , corresponding to the temperature of 551.7 K and 669.4 K, which was the basis of choosing the reduction temperature.

The XPS spectra of the amorphous Ni-B/TiO₂ catalyst before and after reduction were shown in **Figure 1**. In all the samples, two peaks appeared in Ni_{2p3/2} and B_{1 S} levels. Compared with the spectrum of pure nickel metal foil (852.6 eV) and nickel oxide (854.5 eV), on the spectrum of fresh amorphous Ni-B/TiO₂, the peaks at 852.2 eV and 855.5eV in Ni_{2p3/2} level were ascribed to metallic nickel and oxidized nickel, respectively. The metal nickel species increased while oxidized nickel species decreased after the reduction process, suggesting that the oxidized nickel was partially reduced to metallic nickel. High binding energy corresponded to the oxidized state and low binding energy corresponded to the elemental state in the B_{1S} level of fresh and reduced Ni-B/TiO₂. After reduction, the B species was almost not changed. One can see from **Figure 1** that nickel, boron existed both in the elemental and oxidized states on the surface of Ni-B/TiO₂ amorphous catalyst, and all the Ni species almost existed in its oxidized form, which showed that the reduction of oxidized nickel was easier than boron. No significant BE shift of either nickel or boron species was observed, indicating that the electron transfer between Ni and B in Ni-B/TiO₂ amorphous catalyst could be neglected.

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Figure 1 Ni_{2p3/2} and B_{1s} XPS spectra of amorphous Ni-B/TiO₂ samples

(a) freshly prepared; (b) crystal prepared

First, the effect of pre-reduction temperature and reaction temperature on the conversion of TMB on Ni-B/TiO₂ amorphous catalyst was examined using TMB diluted by cyclohexane as reaction liquid. Ni-B/TiO₂ amorphous catalyst showed high activity under different reaction conditions, and TMB can be converted completely when the temperature was above 473 K. This result can be connected with the results of XPS, which showed that Ni-B/TiO₂ catalyst was reduced and its active surface was exposed continually with the increasing of reaction temperature and reaction time.

Then, the activities of Ni-B/TiO₂ and Ni-B/Al₂O₃ amorphous catalysts were compared under the same reaction condition. They all exhibited high activity with the hydrogenation of TMB, but Ni-B/TiO₂ was better. The conversion of TMB was 98.0% on Ni-B/TiO₂ for 7 h, while on Ni-B/Al₂O₃ was 87.9%. So Ni-B/TiO₂ was chosen as catalyst in the hydrogenation of 200# concoctive oil.

The effect of reaction temperature and pressure on the conversion of heavy arenes in petrochemicals was shown in **Figure 2** and **Figure 3**. One can see from **Figure 2** that the conversion of arenes decreased when the reaction temperature was above 433 K. It showed that the hydrogenation of multiple arenes in petrochemicals was difficult. This can be explained that the hydrogenation process of multiple arenes in petrochemicals was very complicated and always accompany with ring opening, isomerization, and so on. **Figure 3** was the results of the reaction pressure effect on arenes conversion. The conversion increased with the reaction pressure, and at last, the conversion was 100 mol% under 3.0 MPa. One can conclude from above result that a favorable condition for the hydrogenation of heavy arenes in petrochemicals on Ni-B/TiO₂ amorphous catalyst was low reaction temperature and high reaction pressure.

Figure 2 The conversion of arenes over Ni-B/TiO₂ amorphous catalyst at different reaction temperature in petrochemicals



Figure 3 The conversion of heavy arenes over Ni-B/TiO₂ amorphous catalyst at different reaction pressure in petrochemicals



Reaction condition: pre-reduction T = 533 K, space velocity = 1 h^1 , P = 3.0 MPa.

Reaction condition: pre-reduction T = 533 K, space velocity =1 h^{-1} , reaction T = 433 K.

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References

- 1. J. A. Schreifels, J. A., P. C. Maybury, W. E. Swartz, J. Catal., 1980, 65, 195.
- 2. H. Yamashita, T. Funabiki, S. Toshida, J. Chem. Soc. Chem. Commun., 1984, 868.
- 3. H. Yamashita, M. Yoshikawa, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans., 1986, 82, 1771.
- 4. M. Shibata, T. Masumoto, Stud. Surf. Sci. Catal., 1987, 31, 353.
- 5. W. Li, K. Y. Tao, Q. Y. Cheng, CN Patent 1 262 147A, 2000, to Nankai University.
- 6. Q. Y. Cheng, W. Li, J. Wu, N. J. Guan, K. Y. Tao, J. Chin. Fuel. Chem. Tech., 2000, 28, 249.

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